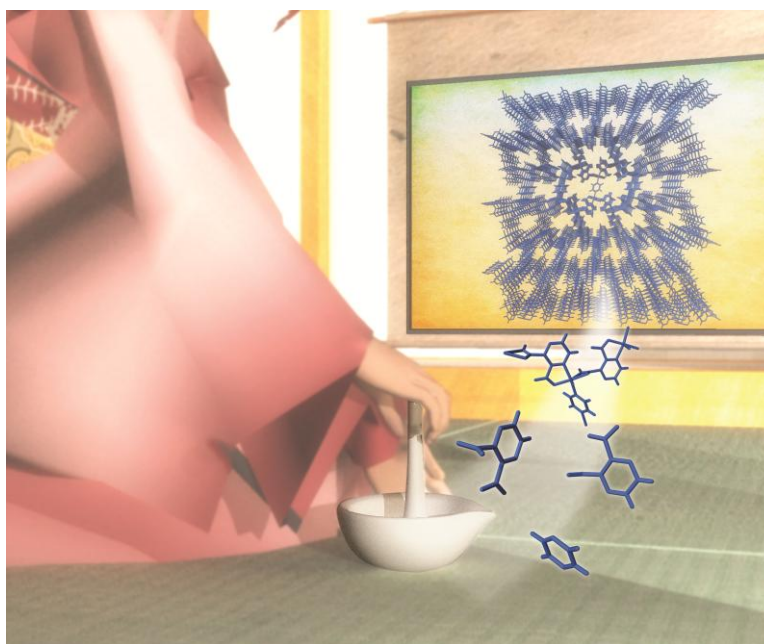


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Coordination chemistry in the solid state

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CO₂ adsorption properties of a Ca(II)-based organophosphonium coordination material†

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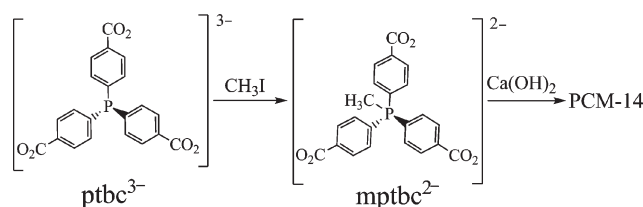
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PCM-14 is a dense coordination polymer formed from Ca(II) and an unusual organophosphonium ligand. The dehydrated framework contains 3-coordinate Ca(II) sites within catenated, chiral 3,3-connected nets. PCM-14 exhibits a stark CO₂ sorption selectivity over H₂, N₂ and O₂. The maximum CO₂ uptake was shown to be highly sensitive to the material pretreatment evacuation temperature.

The development of materials that can efficiently and selectively store gases remains a major challenge for their future relevance in critical applications such as sequestration of CO₂ and other greenhouse gases.¹ Porous coordination polymers are amongst the most promising candidates in this regard, because their sorption selectivity towards small molecule adsorbates is directly tunable as a function of the topology and chemical composition of the micropores.² Recent work in the field has shown that a propitious choice of inorganic and organic components can greatly favour certain types of sorption selectivity. In particular, unsaturated metal sites³ and polar organic moieties⁴ have been shown to favour selective physisorption of small molecules, by promotion of stronger host–guest interactions. For this reason, our continued interest into organophosphine-based coordination polymers has recently focused on studies of the structure–function relationship due to the presence of phosphonium (R₃P⁺–R') ligand-based polar species. It is possible to generate these groups pre-, or post-synthetically by direct reaction of 'free' phosphine-*P* of either the monomer, or a corresponding coordination polymer, with R'I species to yield the corresponding P(v) salt (Scheme 1). Here, the synthesis of a dense framework material with an unusual chiral structure is reported, using pre-synthetically modified [R₃P–Me]Cl in reaction with Ca(II). The metal nodes within this material can be rendered highly unsaturated by removal of three OH₂ ligands per metal. The resulting sorption selectivity with different small molecule adsorbates is reported.

Porous coordination polymers constructed from lighter alkaline-earth metals have been understudied in comparison to the



Scheme 1 Alkylation of the free phosphine (ptbc^{3-} = tris(*p*-carboxylate)triphenylphosphine) with methyl iodide affording the P(v) phosphonium salt (mptbc^{2-} = tris(*p*-carboxylate)triphenylmethyl phosphonium) and the formation of PCM-14.

plethora of examples of *d*-block-based materials, perhaps due to their unpredictable coordination numbers and geometries and limited reactivity.⁵ However, some recently reported Mg(II) frameworks have been shown to result in thermally stable, lighter open-frameworks that are effective in a range of selective gas storage applications.⁶ The Mg(II)-based phosphine coordination material, PCM-11, recently showed an unrivalled CO₂ uptake capacity at high pressure.⁷ Ca(II) centres in porous coordination frameworks should be similarly attractive, and might also offer the possibility to construct unusual framework types due to the expanded coordination sphere. Ca(II) is also comparatively cheap and non-toxic. Relatively few examples of Ca(II) coordination polymers have been reported in the literature.⁵ Plater *et al.* reported the first coordination polymer based on Ca(II), $[\text{Ca}(\text{hbtC})_2\text{H}_2\text{O}]_\infty$, (hbtC^{2-} = benzene-1,3,5-tricarboxylate);⁸ and since then, the vast majority of the Ca(II)-based coordination polymers reported, have focused primarily on the description of the crystal structure.⁹ Only sparse efforts have been made to find different applications for Ca(II)-based coordination polymers, such as catalysis,¹⁰ or water and organic solvent adsorption.¹¹

As shown previously, the trigonal pyramidal geometry of *tris* (*p*-carboxylated) triphenylphosphine results in the rational construction of coordination polymers with *pseudo*-cubic symmetry that have *P*-sites at opposing corners of a cube, with inorganic nodes at alternating corners.¹² In addition, due to the variable oxidation states and coordination numbers available to phosphorus, alkylation of the free phosphine (R₃P) with alkyl iodide (R'I) followed by HCl work-up affords the P(v) phosphonium salt ($[\text{R}_3\text{PR}']\text{Cl}$; Scheme 1) and concomitantly reduces the overall charge on the fully deprotonated ligand from -3 to -2 . Thus, fewer metal cation centres are needed to generate a neutral framework, without altering the geometry and primary function

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† Electronic supplementary information (ESI) available: Additional experimental information, XRPD data corresponding to various pre-treatment conditions, TGA data, and X-ray data. CCDC reference numbers 849683 for PCM-14 (180 K) and 849684 (375 K). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt12011a

of the ligand as a 3-connected node, since the ligand remains tetrahedral at P.

Low-temperature solvothermal reaction of $\text{Ca}(\text{OH})_2$ with the iodo salt of methylphosphonium trylbenzene-*p*-carboxylic acid (mptbcH_3I ; Scheme 1)¹² in slightly basic DMF : EtOH : H_2O (1 : 1 : 1) afforded large crystalline quantities of the complex $[\text{Ca}(\text{mptbc})(\text{OH}_2)_3 \cdot 2\text{H}_2\text{O}]$, hereafter referred to as PCM-14.[‡] Low temperature (-93°C) X-ray structural determination of a single crystal showed that PCM-14 crystallises into the rarely observed chiral cubic space group $I2_13$ ($Z = 8$; Fig. 1A, and associated bond lengths and angles in Table 1).§ The polymer is based on a simple 1 : 1 $\text{Ca}^{2+} : \text{mptc}^{2-}$ ratio and no halide is present. The P1–C1P phosphonium moiety and each Ca1 are resident on 3-fold sites such that only 1/3 of a complete ligand comprises the asymmetric unit. Each phosphonium ligand is coordinated to three symmetry-equivalent Ca1 sites *via* monodentate carboxylate interactions; it is noteworthy that the C7–O1–Ca1 angle is nearly linear at $173.7(3)^\circ$, which suggests a highly ionic interaction *cf.* the expected 120° angle that would be predicted from covalent bonding to an sp^2 -hybridized donor site on carboxylate-O. Ca1 is roughly octahedral with a *fac*-arrangement of carboxylate contacts and three additional *fac*- OH_2 ligands that are partially disordered over two sites in the single crystal at -93°C (Fig. 1A; green bonds). With respect to the overall resulting network type in PCM-14, the ligand provides a 3-connected trigonal node at P1 that bridges to a more uncommon 3-connected node at Ca1, with acute ($92.6(1)^\circ$) angles. Two discrete chiral and catenated 3,3-c nets in PCM-14 (Fig. 1B; pink/blue and green nets) result in a dense material with small pore voids that are occupied by two H_2O solvent molecules per repeat unit.

The framework components themselves are not inherently chiral: the origin of chirality in PCM-14 is a result of “handedness” of each individual 3,3-c network; the bulk of the crystals

Table 1 Selected bond distances (Å) and angles ($^\circ$) for PCM-14

Ca1–O1	2.263(3)	Ca1–O1A ⁱ	2.263(3)
Ca1–O1B ⁱⁱ	2.263(3)	Ca1–O3	2.47(1)
Ca1–O3'	2.271(7)		
O1–Ca1–O1A ⁱ	92.65(12)	O1–Ca1–O1B ⁱⁱ	92.65(12)
O1–Ca1–O3	164.60(4)	O1–Ca1–O3A ⁱ	102.30(4)
O1–Ca1–O3B ⁱⁱⁱ	83.30(2)	O1–Ca1–O3'	173.40(6)
O1–Ca1–O3'A	80.80(6)	O1–Ca1–O3'B	88.80(2)
C1P–P1–C1	109.92(13)	C1–P1–C1A ⁱⁱⁱ	109.02(13)

Symmetry operations used to generate equivalent atoms: (i) $3/2 - z, 1 - x, 1/2 + y$; (ii) $1 - y, 1/2 - z, 3/2 - x$; (iii) $1 - z, x - 1/2, 1/2 - y$; (iv) $1/2 + y, 1/2 - z, 1 - x$.

are therefore expected to be a racemic mixture of enantiomorphous pairs. However, inspection of the extended structure of PCM-14 along (111) clearly shows small cavities flanked by three Ca(II) atoms with a common ‘twist’ direction (Fig. 1C).

To probe the extent to which PCM-14 could be desolvated with the retention of structure, a single crystal was first heated *in situ* to 102°C by a stream of dry N_2 and then allowed to equilibrate for 2 h, before a second X-ray structure was collected.§ We were surprised to find at this temperature that the crystallinity was maintained, but only a proportion of the lattice H_2O molecules had been removed; the coordinated OH_2 also remained intact, but were no longer disordered over two sites. This indicated that both lattice and coordinated H_2O in PCM-14 was strongly bound and would require removal under more forcing conditions.

Thermogravimetric analysis (TGA) of PCM-14 under He carrier gas showed a continuous weight loss of approximately 16.6 wt% over the temperature range 25 – 200°C , which is in agreement with the complete loss of all lattice and coordinated H_2O (calc. 16.8 wt%). PCM-14 reaches a plateau above 200°C with the onset of structure decomposition at 360°C (see ESI Fig. S1†). *In situ* variable-temperature powder X-ray diffraction (PXRD) measurements were used to further probe the dehydration behaviour of PCM-14, upon evacuation at 1×10^{-10} bar at elevated temperatures (Fig. 2). This confirmed retention of the framework up to 200°C , with excellent agreement between the experimental PXRD data and the calculated pattern as simulated from the single crystal data. At 250°C under high vacuum, the material was decomposed.

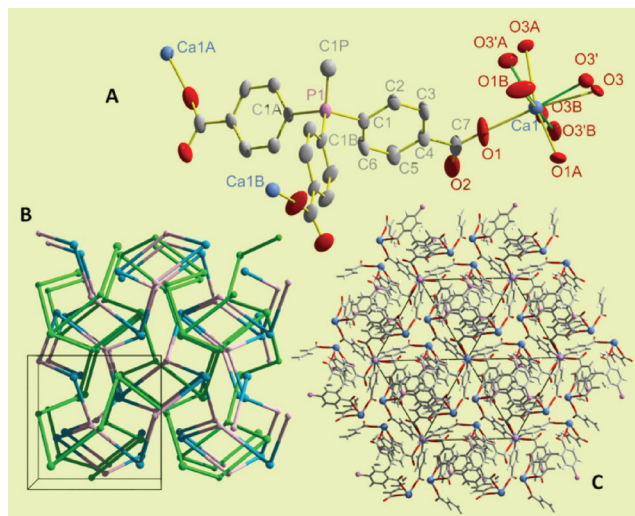


Fig. 1 (A) Expanded asymmetric unit of PCM-14 showing Ca(II) coordination to a single complete phosphonium ligand. Thermal ellipsoids are drawn at the 30% probability level and all hydrogen atoms have been omitted for clarity; (B) representation of the catenated 3,3-connected networks (Ca = blue; P = pink); (C) View of PCM-14 along (111) showing small channels flanked by Ca(II) sites; all water molecules are omitted for clarity.

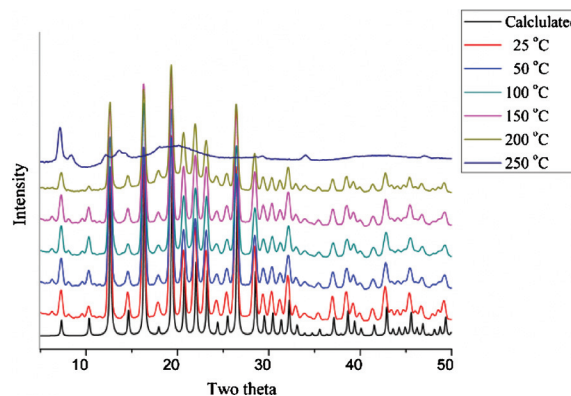


Fig. 2 Variable temperature *in situ* PXRD patterns for PCM-14 and the calculated pattern derived from the single-crystal structure data.

Based on the TGA and XRPD data, it seems reasonable to assume that treatment of PCM-14 under high vacuum at elevated temperature yields the fully desolvated and activated material (PCM-14a). This would invoke the generation of 3-coordinate Ca(II) sites (Fig. 1C) that could potentially enhance gas uptake. Thus, a range of experiments were conducted to study the porosity in PCM-14a. Initial experiments using N₂, H₂ or O₂ at 77 K as the probe gas showed minimal uptake when PCM-14 was pre-activated at 180 °C and 1×10^{-10} bar (0.50 wt%, 0.76 molecules per unit cell; 0.07 wt%, 1.48 molecules per unit cell; 0.39 wt%, 0.52 molecules per unit cell, respectively). However, CO₂ was found to be strongly adsorbed in PCM-14a at 196 K, suggesting a strong selectivity for CO₂ (Fig. 3). CO₂ has a similar kinetic diameter to the other probe analytes, which should equally be able to penetrate the pore openings. A significant desorption hysteresis was also noted for CO₂ (Fig. 3; open green diamonds). There are a number of possible explanations for the observed hysteresis that include the influence of polar P⁺-CH₃ headgroups in the pores. However, the most likely origin of CO₂ trapping in this instance is due to moderately strong physisorption between CO₂ molecules and coordinatively-unsaturated Ca(II) sites. Based on the highly dense nature of PCM-14, the measured pore volume is correspondingly low (0.03 cm³ g⁻¹). To further probe the CO₂ capacity of PCM-14a, freshly-prepared samples were studied as a function of outgassing temperature under vacuum. Samples activated between 25–150 °C and 1×10^{-10} showed no significant CO₂ uptake (approx. 0.16 wt%; Fig. 4), which suggests the presence of coordinated water in the framework.

However, upon increasing the temperature to 170 °C, the uptake rose sharply to 1.74 wt%. This must be due to the barrier for complete dehydration having been reached, and suggests moderately strong Ca-OH₂ coordination in the as-synthesized material. Further increasing the temperature to 180 °C and 1×10^{-10} bar resulted in optimal uptake of 2.92 wt% (corresponding to 2.82 molecules per unit cell). Higher activation temperatures resulted in correspondingly lower CO₂ uptake, most likely due to the onset of structural collapse (Fig. 4). These results were also confirmed by PXRD of the samples after each activation condition (see ESI Fig. S2†). Although PCM-14 is thermally stable up to 360 °C (under He at ambient pressure) and retains overall framework crystallinity up to 200 °C under similar conditions, the vacuum used to evacuate the samples during the activation

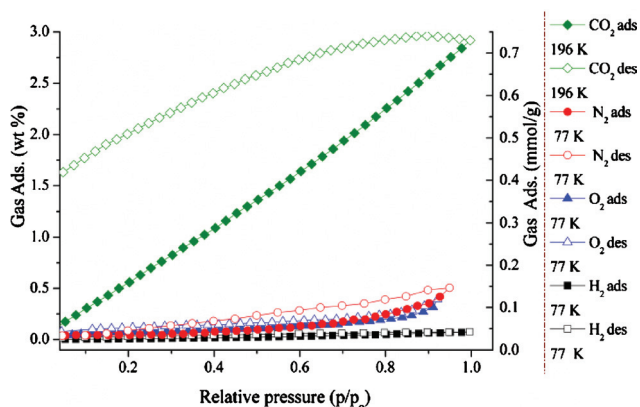


Fig. 3 Adsorption (solid symbols) and desorption (open symbols) isotherms for PCM-14a, desolvated at 180 °C and 1×10^{-10} bar.

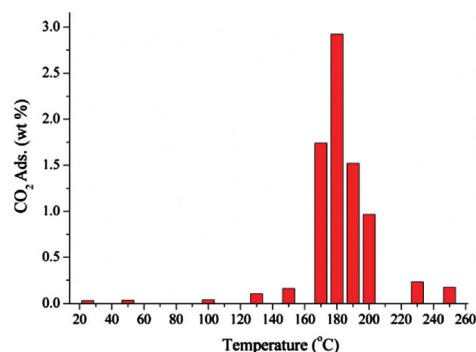


Fig. 4 CO₂ uptake of PCM-14 as a function of different pre-treatment temperatures, at 1×10^{-10} bar.

process may accelerate the degradation of the material.¹³ It is evident from this study that routine exploration of pre-treatment conditions is pivotal to maximization of gas uptake properties in such coordination polymer materials, especially those containing solvated metal sites or other polar framework residues.

Acknowledgements

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Notes and references

† The ligand, [mptbcH₃]Cl, [(H₃C)P(C₆H₅-p-CO₂H)₃]Cl (20 mg, 37 μmol)¹² was dissolved in DMF : H₂O : EtOH (1 : 1 : 1, 2.5 cm³), to which was added a second solution of Ca(OH)₂ (8 mg, 108 μmol) dissolved in 2.5 cm³ of the same solvent. NaOH (0.10 cm³, 1.0 M) was added to the opaque slurry, which was sonicated (20 s). The mixture was then heated in a 20 cm³ sealed glass vial at 70 °C (graphite thermal bath) for 5 days. PCM-14 was formed cleanly and isolated by simple decantation of the supernatant. The crystals were washed with DMF and dried in air prior to activation. (average yield 35 mg, 60% based on Ca). Found: C, 47.9; H, 4.25%; C₂₂H₂₅CaO₁₁P requires: C, 49.2; H, 4.70%; ν_{max} (KBr/cm⁻¹): 1619 m, 1617 m, 1552 s, 1496 w, 1361 s, 1317 m, 1106 m, 1016 m, 901 m, 840 m, 769 s, 734 s, 691 s. After heating a sample of PCM-14 to 50 °C under N₂ for 30 min, Found: C, 50.8; H, 4.42%; C₂₂H₂₃CaO₁₀P requires: C, 51.0; H, 4.47%.

§ Crystal data for PCM-14 (*T* = 180 K): C₂₂H₂₅CaO₁₁P; MW = 532.44, space group *I*2₁3, *a* = 17.1078(9), *V* = 5007.1(5), *Z* = 8, ρ = 1.413 g cm⁻³, *R*₁ = 0.056 (0.091) (4088 independent reflections, *I* > 2σ(*I*)), w*R*₂ = 0.116 (0.135) (all data), GoF = 1.03. Crystal data for PCM-14 (*T* = 375 K) C₂₂H₂₄CaO_{10.5}P; MW = 527.46, space group *I*2₁3, *a* = 17.124 (2), *V* = 5020.9(10), *Z* = 8, ρ = 1.388 g cm⁻³, *R*₁ = 0.059 (0.106) (1292 independent reflections, *I* > 2σ(*I*)), w*R*₂ = 0.143 (0.160) (all data), GoF = 1.04.

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